

Entropies and Heat Capacities of Gaseous Selenium Molecules Se_n ($n = 5 \dots 12$)

Ralf Steudel

Institut für Anorganische und Analytische Chemie, Sekr. C 2, Technische Universität Berlin

Z. Naturforsch. **36a**, 408–409 (1981);
received March 3, 1981

Thermodynamic functions are calculated for gaseous Se_8 molecules from spectroscopic and structural data and listed for temperatures up to 3000 K. Entropy (S^0) and heat capacity (C_p^0) data for Se_n molecules ($n = 5, 6, 7, 9, 10, 11, 12$) are obtained from linear relationships between both S^0 and C_p^0 and ring size n which are derived from the corresponding values of Se_2 and Se_8 .

The presumably cyclic molecules Se_5 , Se_6 and Se_7 are the main constituents of saturated selenium vapor at temperatures up to 400 °C as well as of the vapor above freely subliming trigonal selenium, and cyclic Se_8 molecules can be prepared as various crystalline modifications [1]. Small selenium rings are also discussed as constituents of liquid and amorphous selenium obtained by quenching the liquid or the vapor [1]. To determine the equilibrium concentrations of the various Se_n molecules ($n > 2$) in the liquid and gaseous state, their entropies and heat capacities are needed, but no experimentally determined values have been published so far. Drowart and Smoes [2] as well as Keller et al. [3] calculated the entropies for $n = 3 \dots 8$ using the well known statistically-thermodynamic equations [4] but no information was given concerning the molecular structures and vibrational frequencies used, which had to be assumed since only the molecular structure [5] and vibrational spectra [6–10] of solid Se_8 are known.

The vibrational spectra of Se_8 have recently been assigned and force constants have been calculated [11]. Provided neither the fundamental frequencies nor the structural parameters change on vaporization of the Se_8 molecule, the thermodynamic functions given in Table 1 can be calculated assuming rigid rotator, harmonic oscillator and ideal gas behavior. The obtained entropies differ from the estimated literature data [2] by less than 0.2%. The

principal moments of inertia amount to $I_A = 4380$ and $I_B = I_C = 2410$ (in $10^{40} \text{ g} \cdot \text{cm}^2$; obtained with the structural data cited in [11]).

The molecular structures of Se_8 and S_8 are very similar, and there are many structural parallels between analogous homoatomic sulfur and selenium compounds. The ionization potentials and electron affinities of S and Se atoms are practically identical, leading to identical electronegativities. It is therefore not surprising that eight- and twelve-membered sulfur-selenium mixed rings exhibit the same molecular structures as the corresponding homocyclic sulfur species [12–15]. It, therefore, can be assumed that the cyclic molecules Se_n ($n = 5 \dots 12$) have the same molecular symmetries as the corresponding sulfur rings [16].

The heat capacities (C_p^0) and entropies (S^0) of the sulfur rings S_n ($n = 6, 7, 8, 12$) have been calculated from the known structural and spectroscopic data [18], and it was observed that the values of both C_p^0 and S^0 at a given temperature linearly depend on the ring size n of the molecule S_n . Even the S_2 molecule fits the linear relationships if its entropy is lowered by the contribution of the two unpaired electrons ($9.1 \text{ J/mol} \cdot \text{K}$) [18]. These linear rela-

Table 1. Thermodynamic functions of gaseous cycle-octa-selenium (Se_8 ; symmetry D_{4d}). S_T^0 standard entropy, C_p^0 heat capacity, H enthalpy, G free enthalpy; values in $\text{J/mol} \cdot \text{K}$.

Temp. (K)	S_T^0	C_p^0	$\frac{H_T - H_0}{T}$	$-\frac{(G_T - H_0)}{T}$
100.0	361.2	129.3	80.2	281.0
200.0	464.4	164.4	115.5	348.9
273.2	517.0	172.4	129.8	387.2
298.2	532.2	174.0	133.5	398.7
300.0	533.3	174.1	133.7	399.6
400.0	583.9	177.8	144.3	439.6
500.0	623.8	179.6	151.2	472.6
600.0	656.7	180.6	156.0	500.6
700.0	684.5	181.2	159.6	524.9
800.0	708.8	181.6	162.3	546.4
900.0	730.2	181.9	164.5	565.7
1000.0	749.3	182.1	166.2	583.1
1100.0	766.7	182.2	167.7	599.0
1200.0	782.6	182.3	168.9	613.7
1300.0	797.2	182.4	169.9	627.2
1400.0	810.7	182.5	170.8	639.9
1500.0	823.3	182.5	171.6	651.7
2000.0	875.8	182.7	174.4	701.5
2500.0	916.6	182.8	176.0	740.6
3000.0	949.9	182.8	177.2	772.8

Reprint requests to Prof. Dr. R. Steudel, Institut für Anorganische und Analytische Chemie, Sekr. C 2, Technische Universität Berlin, D-1000 Berlin 12.

tionships allow the estimation of C_p^0 and S^0 values for molecules of intermediate size by interpolation.

Assuming that analogous relationships exist for the cyclic Se_n molecules as well as Se_2 , the following equations can be obtained from the heat capacities and entropies of Se_8 and Se_2 (298 K; entropy of Se_2 lowered by $9.1 \text{ J/mol} \cdot \text{K}$):

$$C_p^0(\text{J/mol} \cdot \text{K}) = 22.17 n - 3.33, \quad (1)$$

$$S^0(\text{J/mol} \cdot \text{K}) = 49.6 n + 135.4. \quad (2)$$

Similar equations can be derived for other temperatures. The C_p^0 and S_{298}^0 values of the molecules Se_n ($n = 5, 6, 7, 9, 10, 11, 12$) calculated from these equations are presented in Table 2. While the entropies calculated this way differ by only 0.2 to 0.8% from the estimated literature data for Se_5 ,

Table 2. Entropies S^0 and heat capacities C_p^0 of gaseous cyclic selenium molecules Se_n at 298 K obtained from equations (1) and (2); values in $\text{J/mol} \cdot \text{K}$.

	S_{298}^0	C_p^0		S_{298}^0	C_p^0
Se_5	383.4	107.5	Se_9	581.8	196.2
Se_6	433.0	129.7	Se_{10}	631.4	218.4
Se_7	482.6	151.9	Se_{11}	681.0	240.5
Se_8	(532.2)	(174.0)	Se_{12}	730.6	262.7

Se_6 and Se_7 [2, 3], the heat capacities for unknown reasons show larger deviations (up to 6%) from the values calculated by Drowart and Smoes [2]. From the experience with sulfur rings [18] it is however concluded that the present data are more reliable.

It has further been found that at given temperatures T_1 and T_2 ($T_1 > T_2$) the function $H_{T_1} - H_{T_2}$ of the sulfur molecules S_2 [2], S_6 , S_7 , S_8 and S_{12} [18] also depends on the number n of atoms in the molecule. For example, the following equation holds for $H_{400} - H_{298}$ (correlation coefficient 0.999):

$$\begin{aligned} \text{S}_n: H_{400} - H_{298} \\ = 2.215 n - 1.196 \quad (\text{in kJ/mol}). \end{aligned} \quad (3)$$

Assuming an analogous relationship for Se_n molecules, a corresponding equation can be derived from the data of Se_2 [2] and Se_8 (Table 1):

$$\begin{aligned} \text{Se}_n: H_{400} - H_{298} \\ = 2.278 n - 0.317 \quad (\text{in kJ/mol}). \end{aligned} \quad (4)$$

Equations of these types allow to calculate $H_{T_1} - H_{T_2}$ for molecules S_n and Se_n ($n = 5 \dots 12$) at any temperatures T_1 and T_2 . It should be pointed out, however, that it may not be allowed to apply equations (1) to (4) to molecules with $n = 3$ or 4 which are likely to be non-cyclic.

- [1] W. C. Cooper and R. A. Westbury, In: R. A. Zingaro and W. C. Cooper (eds.), *Selenium*, Van Nostrand Reinhold Co., New York 1974, p. 87–147.
- [2] Cited in K. C. Mills, *Thermodynamic Data for Inorganic Sulphides, Selenides and Tellurides*, Butterworths, London 1974, p. 78–95 and 725–727.
- [3] H. Keller, H. Rickert, D. Detry, J. Drowart, and P. Goldfinger, *Z. Physik. Chem. Frankfurt* **75**, 273 (1971).
- [4] I. N. Godnow, *Berechnung thermodynamischer Funktionen aus Molekül-daten*, Verlag der Wissenschaften, Berlin 1963.
- [5] R. E. Marsh and L. Pauling, *Acta Cryst.* **6**, 71 (1953); P. Cherin and P. Unger, *Acta Cryst.* **28B**, 313 (1972); O. Foss and V. Janickis, *J. Chem. Soc. Dalton Trans.* **1980**, 624.
- [6] G. Lucovsky, A. Mooradian, W. Taylor, G. B. Wright, and R. C. Keezer, *Solid State Commun.* **5**, 113 (1967).
- [7] G. Lucovsky, In: W. C. Cooper (ed.), *The Physics of Selenium and Tellurium*, Pergamon, Oxford 1969, p. 225.
- [8] R. Zallen and G. Lucovsky in [1], p. 148–173.
- [9] A. Mooradian and G. B. Wright in [7], p. 269.
- [10] R. Laitinen and R. Steudel, *J. Mol. Struct.* **68**, 19 (1980).
- [11] R. Steudel, *Z. Naturforsch.* **30a**, 1481 (1975).
- [12] J. Weiss and W. Bachtler, *Z. Naturforsch.* **28b**, 523 (1973).
- [13] J. Weiss, *Z. Anorg. Allg. Chem.* **435**, 113 (1977).
- [14] C. Calvo, R. J. Gillespie, J. R. Vekris, and H. N. Ng, *Acta Cryst.* **B34**, 911 (1978).
- [15] R. Laitinen, L. Niinistö, and R. Steudel, *Acta Chem. Scand.* **33A**, 737 (1979).
- [16] Molecules Se_n ($n > 8$) have been observed by mass spectroscopy [1, 17].
- [17] H. Saure and J. Block, *Int. J. Mass Spectrom. Ion Phys.* **7**, 145, 157 (1971).
- [18] R. Steudel and H.-J. Mäusle, *Z. Naturforsch.* **33a**, 951 (1978) and references cited therein.